

# Sidewall Functionalization of Carbon Nanotubes\*\*

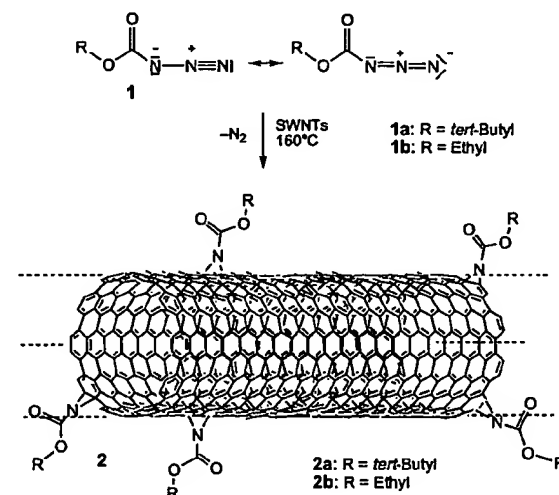
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Carbon nanotubes<sup>[1]</sup> display a wide range of unique electronic, optical, and mechanical properties.<sup>[2,3]</sup> Single-walled nanotubes possess high strain resistance and can be metallic, semiconducting, or insulating, depending on diameter and helicity.<sup>[4]</sup> To be able to apply these properties, chemical derivatization of the nanotubes is desirable to improve their solubility and processability. Such functionalization is interesting, since fundamental knowledge of the chemical properties of nanotubes is thus accessible. Chemical connection of other functional molecules will ultimately lead to new property profiles. Three methods for the exohedral functionalization of carbon nanotubes are open to study: 1) supramolecular complexation of the tube walls with detergents<sup>[5]</sup> and polymers;<sup>[6]</sup> 2) generation and functionalization of defect sites at the tube ends and side walls by oxidation<sup>[6]</sup> and subsequent conversion into derivatives such as amides,<sup>[7]</sup> and 3) direct chemical functionalization of the side walls using addition reactions, of which direct fluorination and subsequent nucleophilic substitution<sup>[8a-d]</sup> and the addition of aryl radicals formed by the reduction of aryl diazonium salts<sup>[8e]</sup> are the only procedures reported to date.

We report here a series of covalent sidewall functionalization reactions and the detailed characterization of the resulting organo-nanotubes. We have selected three types of reaction for direct addition to the unsaturated  $\pi$ -electron system of the nanotubes: 1) the [2+1] cycloaddition of nitrenes; 2) the addition of nucleophilic carbenes, and 3) the addition of radicals. Single-walled nanotubes (SWNTs) were used as starting materials, manufactured either by arc-discharge<sup>[9]</sup> or laser vaporization.<sup>[10]</sup> The SWNT raw material was purified by centrifugation and microfiltration of a dispersion in aqueous detergent solution (sodium lauryl sulfate (SDS) or Triton X 100), then precipitated with ethanol, washed, and dried.

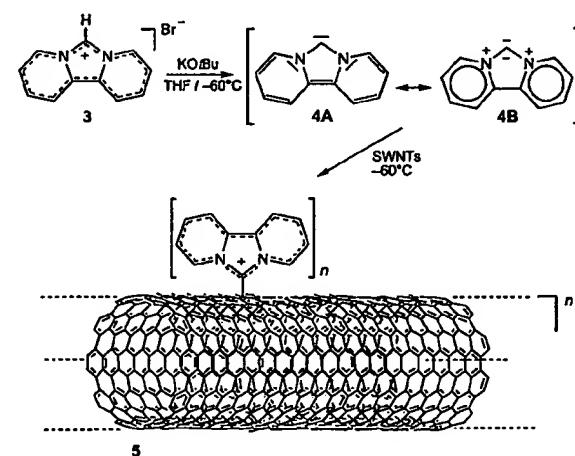
For the addition of nitrenes, the purified SWNTs were redispersed in 1,1,2,2-tetrachloroethane (TCE) in an ultrasound bath under a nitrogen atmosphere over several hours. The suspension was heated to 160 °C and a 200-fold excess of alkyl azidoformate **1a,b** as nitrene precursor was added

dropwise (Scheme 1). After thermally-induced  $N_2$  extrusion from **1**, nitrene addition resulted in the formation of alkoxycarbonylaziridino-SWNTs **2a,b**, which precipitated after a short time. Work-up proceeded by centrifugation and washing of the insoluble residue with diethyl ether. The derivatized SWNTs **2a,b** were soluble in DMSO, which allowed their separation from insoluble contaminants such as starting SWNTs.



Scheme 1. Sidewall functionalization by [2+1] cycloaddition of nitrenes.

The dipyrindyl imidazolidene **4** was selected for the carbene addition. This compound is the prototype "selbststumpfung"-capable, nucleophilic carbene (cf. **4A/4B**).<sup>[11a-d]</sup> Addend **4** is generated smoothly by deprotonation of the dipyrindyl imidazolium system **3** (Scheme 2).<sup>[12]</sup> Compound **4** reacts with electrophilic  $\pi$  systems to give zwitterionic 1:1 adducts rather



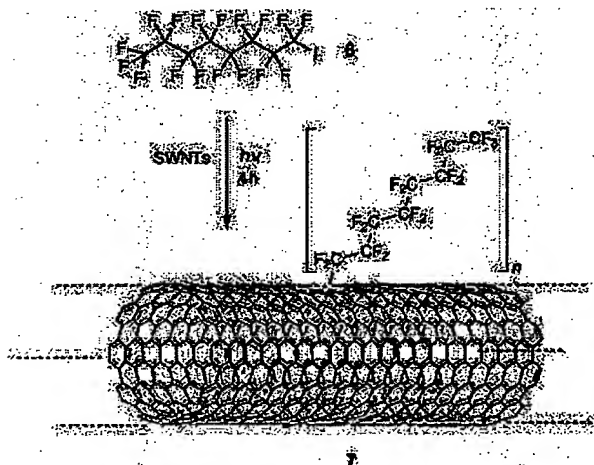
Scheme 2. Sidewall functionalization by the addition of nucleophilic carbenes.

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than cyclopropane systems because of the special stability of the resultant aromatic  $14\pi$  perimeter.<sup>[11a]</sup> The reaction with  $C_{60}$  also gives an adduct of this form.<sup>[11d]</sup> Thus, because of its high nucleophilicity **4** should be well suited for the side-wall functionalization of SWNTs by nucleophilic polyaddition. In the addition reaction, one negative charge per addend is transferred to the tube surface, thus, alteration of the charge offers a further parameter for modifying tube properties (Scheme 2). After filtration through Celite under dry ice/acetone cooling, the freshly prepared, yellow, carbene solution (200-fold excess) was added to a SWNT dispersion in THF at  $-60^\circ\text{C}$ . After stirring at  $-60^\circ\text{C}$  for 3 h, the reaction mixture was slowly warmed to room temperature, then diluted with ethanol. The precipitated functionalized nanotubes **5** were isolated by centrifugation and washed with ethanol. Sufficiently derivatized nanotubes **5** were quite soluble in DMSO, giving a dark solution. This property permitted the separation of the DMSO-insoluble starting and insufficiently functionalized SWNTs by centrifugation. Because of the thermal lability of the adduct, the nanotubes **5** could be investigated by mass spectrometry. By heating a sample to  $50^\circ\text{C}$ , fragments corresponding to bipyridyl ( $m/z$ : 156) and the carbene **4** ( $m/z$ : 168) could be detected as degradation products under electron impact (EI) conditions.

As a reaction of SWNTs with radicals we selected the photoinduced addition of perfluorinated alkyl radicals. For this, SWNTs produced by the arc-discharge technique in the presence of a 200-fold excess of heptadecafluorooctyl iodide **6** dissolved in TCE were illuminated with a medium-pressure mercury lamp (150 W) for 4 h (Scheme 3). Workup was by



Scheme 3. Sidewall functionalization by the addition of a radical.

distillation to remove the solvent and the generated iodine. No difference in the solubility of the fluoroalkyl-substituted nanotubes **7** and the starting materials was observed.

The characterization of products represents a constant problem in nanotube chemistry. In the case of SWNTs, one always works with a polydisperse mixture of tubes or bundles of tubes of differing lengths, diameter, and helicity. The undefined distribution of addends and their addition pattern

over the whole cylinder wall aggravates the problem. In those situations where functionalization is successful, the conjugated double-bond system of the cylindrical surface is interrupted and defect sites will result. An extensive functionalization, this must lead to changes in structure and, therefore, changes in the electronic, optical, and physical properties. For satisfactory characterization of these new classes of substance, data from different measurement methods must be collected and compared. Alongside the standard methods such as NMR and UV/Vis/NIR spectroscopy, the use of atomic force microscopy (AFM) is essential.

The  $^1\text{H}$  NMR spectrum of the Boc-aziridino nanotubes **2a** (Boc = *tert*-butoxycarbonyl Figure 1a) in  $[\text{D}_6]\text{DMSO}$  displays a clear upfield shift of 0.3 ppm and a considerable broadening of the signal of the *tert*-butyl protons compared to that of the corresponding protons in *tert*-butyl azidoformate **1a**. The shift indicates an interaction between the addend protons and the  $\pi$  system of the SWNTs. The signal broadening results from the statistical distribution of the addends on the tube surface. The  $^1\text{H}$  spectrum of the carbene-modified SWNTs **5** (Figure 1b) displays two strong, broadened signals in an intensity ratio of about 1:3. The upfield signal at  $\delta = 7.7$  is assigned to the bipyridyl protons  $\text{H}_a$  of the carbene addend that lies close to the surface of the nanotube. The remaining protons of the bipyridyl subsystem lie further from the carbon tube and come into resonance as a poorly resolved signal at  $\delta = 7.9$ . The signal broadening relative to a methylated reference molecule (Figure 1b) results from the absence of symmetry and of a preferred orientation of the addends relative to the SWNT axis. Furthermore, restricted mobility of these systems in solution is to be expected because of the large size of the nanotubes. These features all contribute to the observed line-broadening. As the radical adducts **7** incorporate fluorinated alkyl chains  $^{19}\text{F}$  NMR spectroscopy can be used to aid characterization. The  $^{19}\text{F}$  NMR spectrum of **7** (Figure 1c), recorded in  $[\text{D}_2]\text{TCE}$ , displays a resonance signal at  $\delta = -80.9$  for the  $\text{CF}_3$  group of C8 and five distinct signals for the  $\text{CF}_2$  groups of C3–7 at  $\delta = -123$ ,  $-124$ ,  $-125$ , and  $-127$ . The signals of the  $\text{CF}_2$  groups of C1 and C2 cannot be assigned. The shielding effect of the nanotube  $\pi$  system has little impact; the signals of the difluoromethylene groups are strongly broadened compared to the starting molecule **6** (Figure 1c).

Nanotubes produced by laser vaporization display characteristic absorption maxima at 650 and 950 nm in their electronic spectra, (Figure 2).<sup>[13]</sup> With the functionalized nanotubes, we find additional absorptions at 1427 nm (for **5**, Figure 2) and 1436 nm (for **2b**, Figure 2,) that are indicative of an alteration of the  $\pi$  system. Overall, however, the absorption behavior in this region was only slightly influenced by modification of the side walls. Even after reaction with carbene **4**, the charge donation to the functionalized SWNTs has no influence on their absorption behavior. Therefore, the addition density and the resulting number of defect sites appears to be very low.

Microscopy is one of the most important methods of characterization in nanotube research. AFM is the best suited method for obtaining authoritative evidence about the sample condition (aggregation, dimensions, and cleanliness), as one

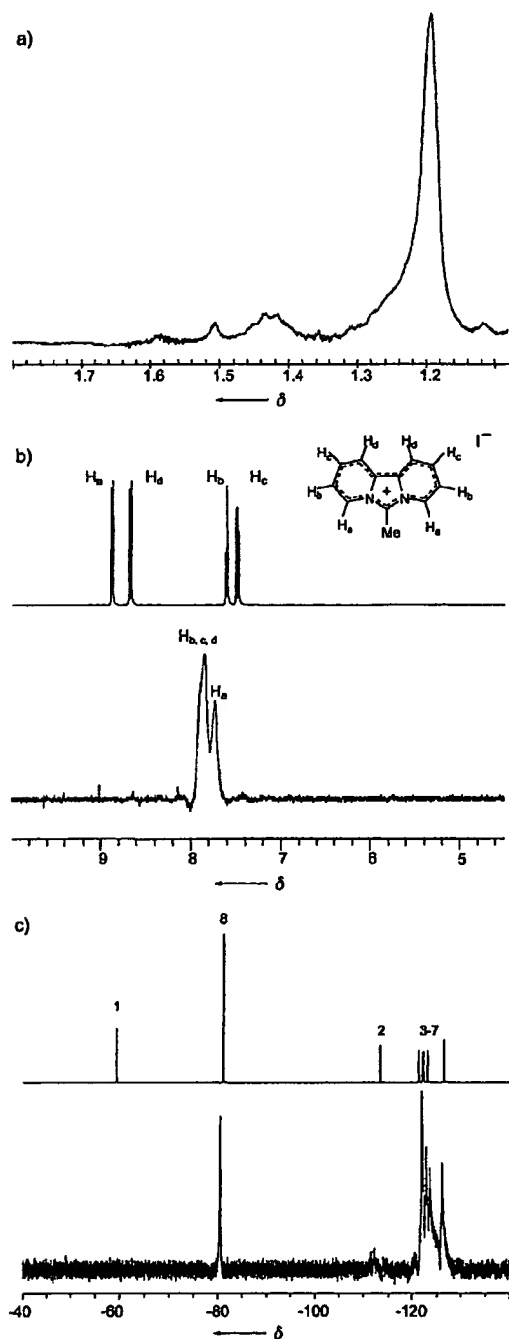


Figure 1. a)  $^1\text{H}$  NMR spectrum of **2a** ( $[\text{D}_6]\text{DMSO}$ , RT); b)  $^1\text{H}$  NMR spectrum of **5** (below) and of dipyrrolo[1,2-c:2',1'-e]-2-methylimidazolium iodide (above) ( $[\text{D}_6]\text{DMSO}$ , RT); c)  $^{19}\text{F}$  NMR spectrum of **7** (below) and the starting materials perfluorooctyl iodide **6** (above;  $[\text{D}_2]\text{TCE}$ , RT).

can observe a relatively large area (Figure 3). Nanotubes obtained by laser vaporization (Figure 3a) order themselves in very large bundles with mean diameters up to 20 nm and are several micrometers long. The analysis of the AFM

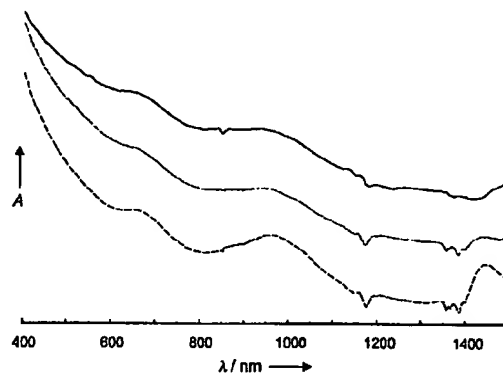


Figure 2. Electronic absorption spectra of purified laser vaporization nanotubes (THF, top curve), **5** from laser vaporization SWNTs (DMSO, middle curve) and **2b** from arc-discharge SWNTs (DMSO, bottom curve).

pictures from functionalized nanotubes showed that, after successful addition of side functionality the bundles were destroyed, so that essentially only individual SWNTs could be observed. This is shown for example in an AFM picture of functionalized nanotubes **2b** (Figure 3b). Their diameter of 2–4 nm, confirmed by the recording of their height profile, corresponds to that of a typical, individual nanotube produced by laser ablation.<sup>[10]</sup> Furthermore, the lengths of the nanotubes remain unaltered after functionalization. The effect of the separation of tubes from the bundles is especially clear to see in the case of the carbene functionalized nanotubes **5** (Figure 3c). Their diameter corresponds to the generally thinner SWNTs obtained by arc-discharge, which have a diameter of 1.3 nm.<sup>[9a]</sup> The height profile (1.0–1.4 nm) of the picture clearly shows the existence of individual, unaggregated SWNTs (Figure 3d).

Both nitrene addition and the carbene addition were carried out with SWNT material obtained by arc-discharge<sup>[9]</sup> and by laser vaporization.<sup>[10]</sup> It appeared that nanotubes made by the laser method were generally better suited for the different functionalizations. In contrast, a partial destruction of the tube structure could be observed when the tubes made by arc-discharge were subjected to nitrene addition. The smaller average diameter results in greater curvature and a larger number of defect sites on the side wall. The number of defects, holes, and amorphous areas in the tube wall causes higher reactivity of the arc-discharge produced tubes and impairs the stability of the tube framework. On the other hand, the defects promote the processibility of the arc-discharge material. Carbon nanotubes made by this method have a lower tendency to form bundles of more than 10 SWNTs and are soluble in significantly higher concentrations in organic solvents. This in turn results in a noticeable improvement in the solubility of the functionalized materials; in the case of the perfluoroalkyl-functionalized SWNTs **7** the solubilities of the starting materials and products were comparable.

With the three different methods of functionalization of the side walls of carbon nanotubes introduced here, the first steps towards general routes to a wide variety of new-nanotube derivatives are presented. With the choice of appropriate

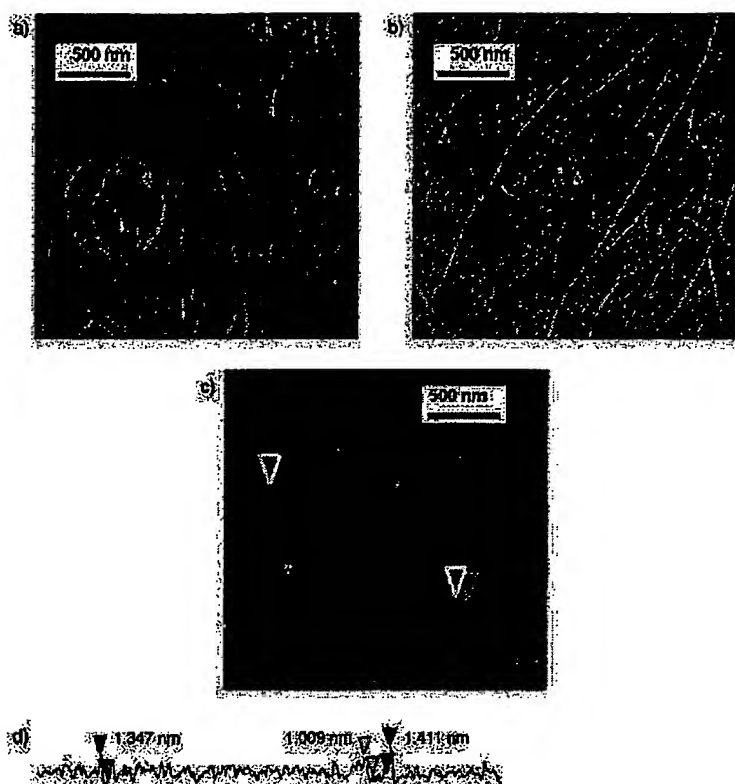


Figure 3. AFM pictures of a) untreated SWNT bundles (from laser vaporization,  $\varnothing$  20 nm), b) individual SWNTs 2h (from laser vaporization,  $\varnothing$  2–4 nm), and c) 5 (from arc-discharge,  $\varnothing$  1.0–1.4 nm). d) Height profile of three functionalized SWNTs 5 (from Figure 3c) with diameters 1.0–1.4 nm.

addends, carbon nanotubes that possess better solubility, are easier to characterize, and feature more straightforward processibility for technological applications are accessible.

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